

# DATA EVALUATION RECORD

## STUDY 8

CHEM 112600 Prohexadione calcium §164-1  
 CAS No. 127277-53-6  
 FORMULATION--14--FLOWABLE CONCENTRATE

### STUDY ID 44457791

Jackson, S. H., D. S. Wesley, and J. R. Patel. 1997. Field dissipation of BAS 125..W in terrestrial use patterns--North Carolina and Texas. BASF Registration Document No.: 97/5060. Unpublished study performed by Agricultural Systems Associates, Cary, NC; and South Texas Agricultural Research, Brookshire, TX (in-life phase); AGVISE Laboratories, Inc., Northwood, ND; and ADPEN Laboratories, Jacksonville, FL (analytical phase); and submitted by BASF Corporation, Research Triangle Park, NC.

### DIRECT REVIEW TIME = 102.5 Hours

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## CONCLUSIONS

### Field Dissipation - Terrestrial

1. This study is scientifically valid and marginally acceptable for fulfillment of the data requirement for a terrestrial field dissipation study for prohexadione calcium use on peanuts. The study shows prohexadione calcium (BAS 125 W; 75 DF), when broadcast applied three times as a spray (21-day intervals) at respective nominal rates of 0.15, 0.15, and 0.30 lb a.i./A to bareground plots of loamy sand soil (NC) and sandy loam soil (TX), dissipated with EFED-calculated linear first order kinetics half-lives of 1 day ( $r^2 = 0.99$ ) and 0.8 day ( $r^2 = 0.89$ ), respectively. It should be noted that a 100-year flood event took place during the field dissipation experiment in NC. Such an event is expected to alter the rates and routes of dissipation for prohexadione calcium and its degradation products. The parent compound (prohexadione calcium) was detected as prohexadione acid. Prohexadione is an acid and it is expected to show some mobility in soil. Prohexadione calcium residues were detected at a depth of 2-4" inches in both the NC and TX sites (see Reviewers' Comments 1).
2. This study is marginally acceptable because the major degradate was not stable in the freezer storage. Because of the instability of the degradate in the freezer storage the study does not provide useful quantitative data to assess the fate and transport of the degradate.
3. The authors stated that prohexadione dissipation was due to degradation in soil. They proposed that prohexadione calcium degrades to despropionyl which degrades further into tricarballic acid and citric acid, both naturally occurring substances. The two acids are subsequently mineralized to  $\text{CO}_2$ , a major terminal product.
4. These field dissipation studies are consistent with the laboratory study findings (the aerobic soil metabolism nonlinear half-life,  $t_{1/2}$ , was 1.4 days with  $r^2 = 0.98$ , while the linear  $t_{1/2}$  was 9.8 days with  $r^2 = 0.73$ ; MRID 44457785). The one day dissipation half-lives are, however, shorter than the 6-20 day half-lives obtained in other dissipation studies. The disparity in half-lives may be due to different environmental conditions, such as rainfall and soil moisture, which could affect the rate of dissipation.
5. No further information is needed on the terrestrial field dissipation of prohexadione calcium at the present time, however, if despropionyl is identified as of toxicological concern than additional data on the degradate will be required.

## METHODOLOGY

**Test Substance:** BAS 125 08 W 75% DF, 74.9% w/w calcium 3,5-dioxo-4-propionyl-3-cyclohexenecarboxylate purity determined by GLP analysis, lot no. AF284-79.

**Field Site and Application of Test Material:** The field trial study was conducted at two sites in North Carolina and Texas, areas representative of the peanut growing regions. BAS 125 W was applied three times in 21-day intervals, at respective nominal rates of 0.15, 0.15, and 0.30 lb a.i./A (120% of the maximum label use rate), onto a bareground plot (89 x 96 ft with five subplots of 9 x 96 ft; 1% slope; p. 59; Figure 2, p. 60) of Kalima loamy sand soil (82% sand, 13% silt, 5% clay, 1.0% organic matter, pH 6.4, CEC 4.4 meq/100 g; Table V, p. 28) in Wayne County, NC (p. 10) and onto a bareground plot (225 x 25 ft with five subplots of 5 x 225 ft; slope 0.7%; p. 62) of Katy sandy loam soil (72% sand, 19% silt, 9% clay, 0.7% organic matter, pH 5.7, CEC 7.2 meq/100 g; Table VI, p. 29) in Waller County, Texas. Plots were bordered with peanuts. The test substance was mixed with the adjuvants AtPlus 111 and urea ammonium nitrate and applied within one hour of mixing using a tractor-mounted boom sprayer (p. 48). The first application occurred 67 days before the harvest of the border crop (in NC at 7/23/96, 8/13/96, and 9/03/96; in TX at 7/09/96, 7/30/96, and 8/20/96). An untreated control plots (NC site: 28 x 90 ft with two subplots of 9 x 90 ft, TX site: 100 x 20 ft with three subplots of 100 x 5 ft) were located 83 and 395 feet from the treated NC and TX plots, respectively.

A three-year plot history indicated no prior use of prohexadione calcium or related compounds (Table X, p. 59, and Table XI, p. 62). Bareground conditions in NC were maintained by two applications of glyphosate (Roundup®, 0.5 lb a.i./A and 1 qt/A) prior to and following the first application of the parent (Tables II, III; p. 46) in TX by one application each of imazethapyr (Pursuit® 2ASU, 0.06 lb a.i./A), pendimethalin (Prowl® 3EC, 0.06 lb a.i./A), trifluralin (Treflan® 4EC, 1.0 lb a.i./A) and metolachlor (Dual®, 2.0 lb a.i./A) prior to treatment; application of glyphosate (Roundup®, 1 qt/A; 3X) and crop oil (1 pt/A; 3X) following the second and third applications of the parent; and application of metolachlor (Dual®, 2 qt/A; 1X) following the third application (p. 46). The seasonal depth to the water table was 12 feet (p. 59) in NC site and 5 to 25 feet in TX site (estimated). Precipitation data were collected on-site (p. 57). Precipitation was supplemented with irrigation (TX site only); total water input (NC site: 19.7 in; TX site: 40.0 in) was 121% in NC site and 242% in TX site (reviewer-calculated) of the 10-year mean annual precipitation for the three months of the study (Table IX, p. 57). Pan evaporation data were not reported.

**Metorological Conditions:** In Appendix B Tables VIII and IX present average monthly air temperatures and precipitation data, respectively.

**Soil Sampling:** Soil samples were randomly collected from the treated plot one day prior to the first application; at 0, 1, 2 (Texas site only), 3 and 20 days following the first application (one day prior to the second application); at 0, 1, 2, 3 and 20 days following the second application (one day prior to the third application); at 0, 1, 2, 3 (Texas site only), 4 (Texas site only), 5, 6, and 7 days following the third application; and at the Texas site only at 13, 17, 21, 34, 59, and 91 days following the third application (Table VII, p. 52). Samples were collected from both control plots prior to each application, at one day following the third application, and from the Texas control plot at 34 and 91 days posttreatment. At each sampling interval, three soil cores were collected from each of the five subplots (total of 15 cores) of the treated and control plots; a 0- to

6-inch depth sample (4-inch i.d.) and a 6- to 48-inch depth sample (1.0-inch i.d. minimum) were collected in two-phases using a zero-contamination probe (p. 51). An additional set of samples was collected from the 0- to 6-inch depth immediately following the third application at the North Carolina site and 1 day following the third application at both sites. The 0- to 6-inch depth soil sample was sectioned into 2-inch increments and the 6- to 48-inch depth soil sample was sectioned into 6-inch increments and the increments were composited by depth and subplot (five samples per composite).

**Application Verification:** A compound application verification was conducted using a petri dish. Fifteen 100 mm petri dishes containing 10 grams of sieved untreated soil were placed randomly in the bare soil plots before applications and collected immediately after. They were analyzed as 5 composites of three together with three spiked composites and three control petri dish composites. In the field, soil samples were transferred from petri dishes to glass amber bottles using DW adjusted to pH 9 with ammonium bicarbonate. The samples were analyzed by ADPEN Laboratories, Inc. They were extracted with ammonium bicarbonate in a shaker at 200-300 rpm and 50 °C for an hour. The extract was filtered through a #4 filter, diluted to known volume with pH 9 water, diluted in 1% acetic acid (1:50 to 1:100) and analyzed via HPLC/UV at 270 nm. Mean corrected recoveries were equivalent to 84-107% of the nominal application rate for the North Carolina site and 101-130% for the Texas site (Table I, p. 16).

**Soil Core Analysis:** The soil samples were analyzed by ADPEN Laboratories, Inc., for BAS 125 W and its metabolite, despropionyl-prohexadione, using high performance liquid chromatography with an ultraviolet detection technique (HPLC/UV detector, BASF Analytical Method No D9607). BAS 125 W and despropionyl were extracted twice from soil samples (20g) by shaking with 0.1 N ammonium bicarbonate in a speed shaker (30 min, at 300 rpm, 50 °C). The combined extracts were centrifuged to remove solids. The obtained supernatants were acidified to pH 2 and cleaned-up using SAX SPE column. The prohexadione residues were eluted with pH-2 water under vacuum conditions. The eluate was divided into two equal aliquots. One aliquot was processed for prehexadione calcium and the second for despropionyl. One aliquot was three times extracted with ethyl acetate after the addition of concentrated sulfuric acid (4 ml) and sodium chloride (20 g). The ethyl acetate extract was filtered with a PS-1 filter with sodium sulfate (50 g). The filtrate was dried, redissolved in 1% acetic acid, and analyzed for prohexadione calcium via HPLC/UV with column switching.

After adjusting pH to 7-8 with 0.5 N sodium hydroxide, the second aliquot was cleaned-up using ENV+SPE column. The despropionyl residue was eluted from column with water (25 ml) under vacuum. The purified eluate's pH was adjusted to pH 2 with sulfuric acid and the eluate was cleaned-up again via ENV+SPE column. The column was eluted with ethyl acetate (15 ml). The obtained eluate was extracted twice with 0.5 N sodium hydroxide. The aqueous fraction was diluted to 10 ml, acidified to at least pH 2, and analyzed for despropionyl (KI-5376) via HPLC/UV (column switching).

All soil sample residues were corrected for soil moisture content but were not corrected for procedural recoveries. This method assures  $78.1 \pm 10.93\%$  ( $n=152$ ) average procedural recoveries of BAS 125 W in soil,  $83.3 \pm 9.62\%$  ( $n=39$ ) of prohexadione, and  $77.4 \pm 12.1\%$  ( $n=530$ ) of despropionyl. For this method the limit of quantitations (LOQ) are 0.01 ppm for both BAS 125 W and its degradate despropionyl.

**Sample Storage and Stability:** Soil samples were shipped in a freezer truck to BASF Corporation in RTP, NC. After processing the sample aliquots were shipped frozen, in insulated containers with dry ice, from BASF to ADPEN Laboratory for analysis. In this study samples were stored frozen (0 to  $-22^{\circ}\text{C}$ ) for a maximum of 13 months until analysis (p. 13; Table IXb, p. 33). BAS 125 W has been stable in the frozen state on soil for up to 17 months (see Study 11, 44725215) while despropionyl was not stable in freezer storage (see Study 10, MRID 44725214). Despropionyl samples fortified at 1.00 ppm degraded to 0.7 % of their original concentration during 12 months of storage. Within the first 21 days of storage about 80% of despropionyl degraded.

To determine transit stability, samples (20 g) of sieved (1 mm) control soil from each site were fortified in the field at 0.4 ppm with prohexadione calcium and transported with field soil samples (p. 102). Mean corrected recoveries were  $86 \pm 8.4\%$  for the North Carolina site and  $93 \pm 11.1\%$  for the Texas site (Tables 3.a-b, pp. 129-130).

**DT<sub>50</sub> Calculations:** The concentrations were calculated by averaging the three replicates of each depth interval for each sampling period and then summing the depth interval averages. The summed concentration for each sampling period was then analyzed by nonlinear regression of the natural log of the concentration relative to time. Concentrations  $<0.01$  were considered to be zero for purpose of regression calculation. Nonlinear regression and the calculation of DT<sub>50</sub> and DT<sub>90</sub> determined from the following equation:

$$\ln C = \ln C_0 - \alpha \ln(1 + \beta t),$$

where  $C_0$ ,  $\alpha$ , and  $\beta$  are solved for in sequence as unknowns, after transforming the concentrations. Dissipation times are then calculated by:

$$\text{DT}_{50} = [0.5^{-(1/\alpha)} - 1] / \beta$$

$$\text{DT}_{90} = [0.1^{-(1/\alpha)} - 1] / \beta$$

$\alpha$  and  $\beta$  are determined by using Coplot Scientific Graphics Software.

**Solution Movement:** Graphical presentations of correlation between residue mobility and soil water recharge events were performed. Soil solution movement was calculated from the following algorithm:

$$\text{Surface layer } \Delta \Theta = \sum_i^{t=1} [(P + SM + I) - (Q - ET_c)]$$

$$\Delta \Theta = \sum_i^{t=1} [Inf - RFc]$$

Subsurface layer

t time [days]

$\Theta$  soil matrix water content

P precipitation

SM snow melt (when the snow pack exists and the ambient temperature is  $\geq 32$  °F)

I irrigation

Q runoff

ETc evapotranspiration corrected for the crop ( $ETc = ET * Kc$ ); with  $Kc = 0.64$  to  $0.84$

Inf infiltration

RFc root extraction factor  $RFc = RF * c$ ;  $c = 1.0$

#### STUDY AUTHORS' DATA SUMMARY:

Table I presents the application verification results and Table II the zero-time core concentrations. The application verification recovery rates ranged from 84% to 130%. The zero-time core recoveries were 69% (TX) and 106% (NC). Both the petri dish results and the zero time core recovery data showed that the application was accurate and precise.

Prohexadione calcium (BAS 125 W; 75 DF), broadcast applied three times as a spray (21-day intervals) at respective nominal rates of 0.15, 0.15, and 0.30 lb a.i./A to bareground plots of loamy sand soil (NC) and sandy loam soil (TX), dissipated with registrant-calculated half-lives (reported as  $DT_{50}$ 's derived from nonlinear regression) of 1.0 day ( $r^2 = 0.99$ ; p. 17; Figure 1, p. 18) and 0.78 days ( $r^2 = 0.91$ ; p. 17; Figure 2, p. 18), respectively. The parent compound (prohexadione calcium) was detected as prohexadione acid.

Table VII and VIII present BAS 125 W soil residues (also see soil sample collection day corrections Table VII, p. 52). The data indicate that prohexadione calcium was not detected below 4 inches and was only detected in three instances at 2 to 4-inch depths (single replicates at concentration no more than 0.266 ppm, LOQ =  $<0.01$  ppm). The authors' review of graphical display of soil residue data by depth, with time, and soil solution transport by depth, with time, implies that although soil solution leached past 48 inch rootzone, prohexadione calcium did not move past 4 inch soil depth..

Due to a freezer storage instability (Table IX), the major degradate, despropionyl, was not detected in any site in this study. In a different study, however, it was detected in all sites for up to 10 to 21 days and at a maximum concentrations of 0.025 to 0.041 ppm (Jackson et. al, 1998; MRID 44725213). In that study the prohexadione calcium application rates were higher allowing for degradate detection before it was all lost in storage.

### North Carolina Site

The parent was present in the 0- to 2-inch depth at 0.092 ppm immediately following the first application and was not detected by 20 days posttreatment (one day prior to the second application; Table VII, p. 30; see Comment #9). The parent was present at 0.062 ppm immediately following the second application and was not detected by 3 days posttreatment (18 days prior to the third application). The parent was present at 0.31-0.38 ppm immediately following the third application, decreased to 0.17-0.22 ppm by 1 day and 0.13 ppm by 2 days posttreatment, was not detected at 5 days and was present at 0.011 ppm (one of three replicates) at 7 days posttreatment. The parent was detected once in the 2- to 4-inch depth at 0.27 ppm (one of six replicates) at 1 day following the first application and was not detected below the 2- to 4-inch depth. The degradate despropionyl prohexadione was not detected at any sampling interval or depth (EFED notes that the degradate even present could not be detected due to prolonged samples storage and despropionyl instability under the storage conditions, p. 127).

### Texas Site

The parent was present in the 0- to 2-inch depth at 0.14 ppm immediately following the first application and was 0.026 ppm at 20 days posttreatment (one day prior to the second application; Table VIII, p. 31). The parent was present at 0.11 ppm immediately following the second application and was not detected by 20 days posttreatment (one day prior to the third application). The parent was present at 0.12-0.25 ppm immediately following the third application, decreased to 0.076-0.077 ppm by 1 day and 0.028 ppm by 3 days posttreatment, and was last detected at 0.012 ppm (one of three replicates) at 4 days posttreatment. The parent was detected twice in the 2- to 4-inch depth at 0.017-0.041 ppm (two of three replicates) at 3 days following the second application and at 0.012 ppm (one of six replicates) at 1 day following the third application, and was not detected below the 2- to 4-inch soil depth. The degradate despropionyl prohexadione was not detected at any sampling interval or depth ((EFED notes that the degradate even present could not be detected due to prolonged samples storage and despropionyl instability under the storage conditions, p. 128).

## THE REVIEWERS' COMMENTS

1. The study shows prohexadione calcium (BAS 125 W; 75 DF), when broadcast applied three times as a spray (21-day intervals) at respective nominal rates of 0.15, 0.15, and 0.30 lb a.i./A to bareground plots of loamy sand soil (NC) and sandy loam soil (TX), dissipated with EFED-calculated half-lives of 1 day ( $r^2 = 0.99$ ) and 0.8 day ( $r^2 = 0.89$ ), respectively. Prohexadione calcium residues were detected at a depth of 2-4" inches in both the NC site (one replicate of 0.266 ppm at 1 day after 1<sup>st</sup> application) and in the TX site (two replicates of 0.017 ppm and 0.042 ppm at 3 days after 2<sup>nd</sup> application, and one replicate of 0.012 ppm at 1 day after last application) in all cases but one above the LOQ. The residue detections immediately after treatment in the NC and TX sites, however, are most likely due to sample contamination and not leaching. No residues were detected

below 4 inches at concentrations  $\geq 0.01$  ppm. Degradate despropionyl prohexadione was not detected in any of the study sites (LOQ = 0.01 ppm).

2. The linear half-lives in these field dissipation studies of 1 day ( $r^2 = 0.99$ , NC) and 0.8 day ( $r^2 = 0.89$ , TX) are consistent with to the laboratory study findings (aerobic soil metabolism non-linear  $T_{1/2} = 1.4$  days with  $r^2 = 0.98$ , linear  $T_{1/2} = 9.8$  days with  $r^2 = 0.73$ ; MRID 44457785) and much shorter than those of the field dissipation studies conducted in CA, OR, and NY (non-linear  $T_{1/2}$  of 15, 20, and 5.7 days in the NY, CA, and OR bare soil plots, MRID 44725213). It is speculated that the disparity could be due to the difference in soil moisture. In the NC site when a rain deficit in July and August took place (time of 1<sup>st</sup> and 2<sup>nd</sup> application) the BAS 125 soil residues had significantly longer residence time in the soil than in September (3<sup>rd</sup> application). (Linear  $T_{1/2}$  1<sup>st</sup> application = 9.6 days and  $T_{1/2}$  2<sup>nd</sup> application = 6.7 days vs  $T_{1/2}$  3<sup>rd</sup> application = 1.0 days; NC applications dates were: 7/23/96 - 1<sup>st</sup>, 8/13/96 - 2<sup>nd</sup>, and 9/03/96 - 3<sup>rd</sup>; see Comments 4 and 7). In September, however, a 100-year flood event took place (the total precipitation for Sep. was 13.45 vs 4.35 the 14-year avg. historical precipitation) after which the parent was not detected at 5 days posttreatment. This storm event could have an impact on the field dissipation rate. The first and second application half-lives in NC are in the range of the laboratory half-lives. Much lower treatment rates used in NC and TX sites than those in the CA, OR, and NY sites could contribute to the half-life disparity between the two types of field dissipation studies. The field data generated in the CA, OR, and NY studies had high variability.
3. The major degradate, despropionyl prohexadione, was not stable in the freezer storage and thus was not detected in the study. The study does not provide useful quantitative data to assess the fate and transport of the degradate. To avoid loss of the degradate in the storage the samples supposed to be analyzed immediately after sampling.
4. In the NC site, the monthly rainfall data (Table IX) indicate a rain deficit in July and August which could result in low soil moisture content and thus prohibit the compound from leaching. During these months the BAS 125 soil residues had significantly longer residence time in the soil ( $T_{1/2}$  1<sup>st</sup> application = 9.6 days,  $T_{1/2}$  2<sup>nd</sup> application = 6.7 days) than in September, when a 100-year flooding event occurred (see Comment #7). In conclusion, the Agency believes the weather conditions at the NC site are atypical and hence the interpretation of the NC data is limited. The study report did not included the pan evaporation data at either site and any daily records of environmental conditions (i.e., temperature, rainfall, etc.). In future studies the registrant should provide water balance data for each field dissipation study.
5. The soil cores for the 6- to 48-inch depth were reported to be a minimum of 1-inch in diameter (p. 51). Soil cores of 1-inch in diameter may not provide representative samples.



6. Method validation data were not submitted. Subdivision N Guidelines require that method validation data for the analytical methods be submitted for newly registered chemical.
7. Characteristics of the irrigation water were not reported.
8. At the North Carolina site, soil core samples were not collected at 3 and 4 days posttreatment due to rain from a hurricane and samples could not be collected following the 7-day posttreatment sampling interval because the site was completely flooded due to a 100-year flood event (p. 67). The parent was not detected at 5 days posttreatment and was detected at 0.011 ppm (one of three replicates) at 7 days posttreatment. The inability to collect samples may not have negatively affected the study based on the rapid degradation of the parent observed prior to the flooding.
9. The formulation of the pesticide was reported as dry flowable (p. 9), for which no formulation code was available; therefore, the reviewer reported it as flowable concentrate (formulation code 14).

#### REFERENCES:

Jackson, S. H., Wesley, D.S., and J.R. Patel. November 25, 1998. Amended Final Report: Field dissipation of BAS 125 W in orchard use patterns - NY, CA, and OR. Submitted by BASF Corporation. RTP, NC. BASF Reg. Document No. 98/5199 and Protocol No. 96015 (Amended Final Report). 3 volumes, 1070 pp.

McCall P.J., Swann R.L., Laskowski D.A., Unger S.M., Vrona S. A. and Dishburger H.J. Estimation of Chemical Mobility in Soil from Liquid chromatographic Retention Times. 1980 *Bull. Environ. Contam. Toxicol.* **24**, pp190-195.

Prohexadione Calcium

DER MTD 44457791

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Pages 10 through 27 are not included.

The material not included contains the following type of information:

- ☐ Identity of product inert ingredients.
- ☐ Identity of product impurities.
- ☐ Description of the product manufacturing process.
- ☐ Description of quality control procedures.
- ☐ Identity of the source of product ingredients.
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